FINAL PROGRESS REPORT (ORIGINAL AND TWO COPIES REQUIRED)

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TITLE OF PROPOSAL:	Rydberg States of Energetic Materials
NAME OF INSTITUTION:	Colorado State University
AUTHOR OF REPORT:	Elliot R. Bernstein

STATEMENT OF PROBLEM

In this work we studied the fragmentation, reactions, and dynamics of model energetic compounds (methyl amines, azaaromatics, radicals) with high excitation energies. The general idea was to characterize the behavior of electronically excited energetic materials and to understand the beginnings of the decomposition processes.

SUMMARY OF MOST IMPORTANT RESULTS

The main results of the last three years are well represented in the Technical Progress Reports already submitted. These studies show that radicals and Rydberg states play an important role in the fragmentation behavior and dynamics of many energetic materials model systems. We have generated new and never-before studied radicals of substituted cyclopentadienyls (CN, F, CH_3) and lutidyl and picolyl and have shown that their excited electronic states are much more reactive than their ground states. We have demonstrated their reactivity toward small substituted methanes, water, alcohol, ammonia, and others. We have developed now published algorithms for the theoretical description of such behavior.

The latest progress of the last six months of this effort (since our last comprehensive report of results and progress) has been for laser ablation of RDX and related materials. We have now constructed a supersonic nozzle that can be used with laser ablation of matrix isolated materials. The nozzle works well with large molecules and metal oxide systems, and we can observe the original molecule as well as its fragments in the mass spectrum of the ablated material. We have observed V_xO_y, Ti_xO_z, tyramine, tryptamine, dopamine, and other large involatile molecules as well as their fragments in this manner. Covariance mapping of these ablation plumes has given us good information on how molecules and clusters can fragment.

All of these results are published, with the exception of the metal oxide and organic molecule ablation results. These are reported here for the first time. The fact that we can now access such diverse systems from matrices for mass spectroscopy and covariance mapping is a major step forward for our program with ARO.

LIST OF PUBLICATIONS AND TECHNICAL REPORTS

Interim Progress Report for 1/1/97 – 12/31/97 period
Interim Progress Report for 1/1/96 – 12/31/96 period
Interim Progress Report for 4/15/95 – 12/31/95 period
R. Disselkamp, Q. Y. Shang and E. R. Bernstein, "A CASSCF Study of the Ground State and Lowest Lying 3s Rydberg States of ABCO," *J. Phys. Chem.* **99**, 7227 (1995).

E. R. Bernstein, "Dynamics and Photochemistry of Neutral van der Waals Clusters," *Ann. Rev. Phys. Chem.* **46**, 197 (1995).

S. Sun and E. R. Bernstein "Vibronic Structure of the Cyclopentadienyl Radical and its Nonrigid van der Waals Cluster with Nitrogen," *J. Chem. Phys.* **103**, 4447 (1995).

C. F. Dion and E. R. Bernstein, "On the Low Lying Rydberg States of Azabenzenes," *J. Chem. Phys.* **103**, 4907 (1995).

E. R. Bernstein, "Intermolecular Dynamics and Bimolecular Reactions," in *Chemical Reactions in Clusters* E. R. Bernstein (Ed.) (Oxford, New York, 1996) pp. 147.

D. P. Taylor and E. R. Bernstein, "On the Low Lying Excited States of Methyl Amine," *J. Chem. Phys.* **103**, 10453 (1995).

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C. F. Dion and E. R. Bernstein, "Electron Transfer Reactions in Clusters: The Effect of Polar Solvents on the (2p3s) Rydberg State of Azabicyclooctane," *J. Chem. Phys.* **104**, 2891 (1996).

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J. A. Bray and E. R. Bernstein, "On the Barriers to Internal Rotation in Methyl Substituted Pyridines," *J. Chem. Phys.* submitted.

J. Yao and E. R. Bernstein, "On the Formation and Vibronic Spectroscopy of α-Halobenzyl Radicals in a Supersonic Expansion," *J. Chem. Phys.* **107**, 3352-3362 (1997).

J. A. Fernandez, J. Yao, and E. R. Bernstein, "Solvation of the Methoxy Radical in Small Clusters," *J. Chem. Phys.* **107**, 3363-3375 (1997).

J. Yao, J. A. Fernandez, and E. R. Bernstein, "On the $\tilde{A}$ and $\tilde{B}$ Electronic States of NCO and its Clusters with Nonpolar Solvents," *J. Chem. Phys.* **107**, 8813 (1997).

J. Fernandez, J. Yao, J. A. Bray, and E. R. Bernstein, "Solvation of Radicals in Small Clusters," in *Structure and Dynamics of Excited States*, J. Laane, Ed. (Springer-Verlag) in press.

J. Fernandez, J. Yao, and E. R. Bernstein, "Solvation of Cyclopentadienyl and Substituted Cyclopentadienyl Radicals in Small Clusters: I. Nonpolar Solvents," *J. Chem. Phys.*, submitted.

J. Yao, J. Fernandez, and E. R. Bernstein, "Solvation of Cyclopentadienyl and Substituted Cyclopentadienyl Radicals in Small Clusters: II. Cyanocyclopentadienyl with Polar Solvents," *J. Chem. Phys.*, submitted.

J. Fernandez, J. Yao, and E. R. Bernstein, "Solvation of Cyclopentadienyl and Substituted Cyclopentadienyl Radicals in Small Clusters: III. Pre-Reactive Clusters," *J. Chem. Phys.*, submitted.

M. Foltin and E. R. Bernstein, "Two Photon Spectroscopy of Water," *J. Chem. Phys.*, to be submitted.

M. Foltin, G. Stueber, and E. R. Bernstein, "Dynamics of Neutral Cluster Growth and Cluster Ion Fragmentation for Toluene/Water, Aniline/Argon, and 4-

Fluorostyrene/Argon Clusters: Covariance Mapping of the Mass Spectral Data," *J. Chem. Phys.*, **109**, 4342 (1998).

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J. A. Bray and E. R. Bernstein, "3-Picolyl and 2,5-Lutidyl Radicals: Generation, Optical Spectroscopy, and Ab Initio Calculations," *J. Chem. Phys.*, accepted.

J. A. Bray and E. R. Bernstein, "Solvation of the 2,5-Lutidyl Radical in Small van der Waals Clusters," *J. Chem. Phys.*, accepted.

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12. ABSTRACT (*Maximum 200 words*) Energetic materials are modeled experimentally and theoretically with regard to possible excited electronic Rydberg state reactivity and dissociation. The systems of methyl and ethyl alkyl amines have been studied. We show that these Rydberg states can be both highly reactive and dissociative. Thus, excited Rydberg states are a possible route to radicals and other reactive species for these model systems. We are presently expanding our experimental capabilities to allow study of broad spectra of model energetic materials such as nitramines and nitro compounds in general.

Studies employing covariance spectroscopy of clusters are used to demonstrate the importance of this technique for finding parent/daughter relations in fragmentation studies. Radical behavior is investigated as it relates to fragments of energetic materials.

14. SUBJECT TERMS Energetic materials, RDX, Rydberg states, radicals, covariance mapping, fragmentation studies, laser ablation

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